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(19) (CA) APPLICATION FOR CANADIAN PATENT (12)

(54) Method of Lubrification Treatment for Cold Working of
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Notice: The specification contained herein as filed

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Abstract of the Disclosure

An improved lubricating layer for heavy cold working of iron and steel objects can be obtained by first phosphating them with a solution comprising, in percentages by weight, 0.3 to 2.5 % of zinc ions, 0.01 to 2.0 % of ferrous ions, 0.5 to 5.0 % of phosphate ions, 0.7 to 12.0 % of nitrate ions, and 0.02 to 0.25 % of water soluble aromatic organic compounds that contain both nitro and sulfonic groups, with the ferrous ion and zinc ion contents additionally being such that the weight ratio of ferrous ions to zinc ions in the phosphating solution is within the range from 0.005 to 3.0. Optionally, the phosphating solution may also contain from 0.2 to 2.0 % of calcium ions, and when it does, the weight ratio of calcium ions to zinc ions in the solution should also be in the range from 0.7 to 4.0. After phosphating, the phosphated surfaces are treated with a conventional lubricant, preferably a weakly alkaline solution of sodium stearate.

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IMPROVED METHOD OF LUBRICATING IRON AND STEEL BEFORE COLD
WORKING

Field of the Invention

This invention relates to a method for forming an improved lubricating layer optimized for cold plastic working, e.g., drawing of tubing and wire, forging, header working, and the like, on the surface of objects made of iron and steel, e.g., low- and high-carbon steels, low alloy steel, and the like. The first major stage of the method is a phosphating treatment with an optimized composition of phosphating solution.

10 Description of Related Art

When iron or steel is subjected to cold plastic-working (generally denoted herein below simply as "cold working"), the surface of the workpiece is usually first subjected to a lubrication treatment in order to reduce tool wear and seizure between the workpiece and tool. In the case of relatively light cold-working operations, this lubrication treatment conventionally consists of coating the surface of the article with an oil which contains an extreme-pressure additive or lubricity improver. In the case of severe cold-working operations, a widely practiced

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method consists of the formation of a zinc stearate lubricant layer over a zinc phosphate-based film and the additional formation of a sodium stearate layer over this zinc stearate layer. This may be achieved, for example, by dipping the article to be lubricated into a zinc phosphate based conversion treatment solution (containing sodium nitrite as accelerator) heated to 70 to 80 degrees Centigrade, followed by, for example, dipping in a sodium stearate based metal soap solution (for example, Palube® 235 from Nihon Parkerizing Company, Limited, Tokyo) heated to 70 to 75 degrees Centigrade. Moreover, research has been carried out on improving the base film with the objective of improving the performance of such lubricant coatings, and results in this regard have been disclosed in Japanese Patent Publication Number 60-20463 (alternatively numbered 20,463/85). The conversion treatment in the aforesaid invention is conducted at approximately 80 degrees Centigrade using a zinc and calcium phosphate based treatment solution with specified component concentrations.

When these two types of base layer treatments as known in the prior art are examined, it is found that they both suffer economically from needing a relatively high conversion treatment temperature and from the generation of relatively large quantities of sludge in the phosphating treatment bath.

It is an object of the present invention to achieve a reduction in both treatment temperature and sludge formation compared with that known in the prior art, and it is another object of the invention to achieve an improvement in the performance and quality of the film obtained as a base layer for a final cold working lubricant layer.

Description of the Invention and Drawings

Except in the operating examples, or where otherwise expressly indicated, all numerical quantities in this description indicating amounts of material or reaction conditions are to be understood as modified by the word "about".

It has now been found that the temperature of a phos-

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phating treatment bath can be lowered into the range of 35 to 65 degrees Centigrade, that sludge production during phosphating could be substantially reduced, and that a lubricant film which has a better resistance to cold working than in the prior art could be formed after phosphating, through the addition to an otherwise conventional ferrous ion containing phosphate treatment solution of moderately oxidizing, water-soluble, aromatic compounds containing both nitro and sulfonic groups, such as the alkali metal salts of nitrobenzene sulfonic acid, nitroaniline sulfonic acid, nitrotoluene sulfonic acid, and/or nitroxylenesulfonic acid, while at the same time using the other components in the treatment solution at specified concentrations and within particular ranges of composition with respect to each other, as specified below. Specifically, the phosphating solution for use in this invention should contain, in percentages by weight as are all percentages given herein unless otherwise specified, 0.3 to 2.5 % of zinc ions, 0.01 to 2.0 % of ferrous ions, 0.5 to 5.0 % of phosphate ions, 0.7 to 12.0 % of nitrate ions, and 0.02 to 0.25 % of water soluble aromatic organic compounds that contain both nitro and sulfonic acid or sulfonate salt groups, with the ferrous ion and zinc ion contents additionally being such that the weight ratio of ferrous ions to zinc ions in the phosphating solution is within the range from 0.005 to 3.0. Optionally, the phosphating solution may also contain from 0.2 to 2.0 % of calcium ions, and when it does, the weight ratio of calcium ions to zinc ions in the solution should also be in the range from 0.7 to 4.0. Also optionally, the phosphating solution to be used for this invention may additionally contain a chelating agent for ferrous ions, chlorate ions, and heavy metal cations such as nickel, cobalt, manganese, or copper. Preferably the phosphating solutions consist essentially of only water, the other constituents named above, and any necessary counter ions for the ionic constituents.

In a process according to the invention, the iron or

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steel object to be treated is contacted with a phosphating solution as noted above for a time of from 3 to 20 minutes at a temperature of from 35 to 65 degrees Centigrade. A final lubricating film is then formed by treating the phosphate film thus formed by methods conventional in the art for treating zinc phosphate based films to produce lubricant films for cold working. Even though the methods used for forming the lubricating layer are conventional, the resulting layer gives superior lubrication, apparently as a result of favorable interactions with the phosphating layer deposited by a method according to this invention.

Considering the invention in greater detail, the phosphating solution used comprises zinc ions and ferrous ions as its essential cationic components. The zinc ion is to be present at 0.3 to 2.5 %, because the formation of a film suitable for cold working becomes problematical at a zinc ion concentration below 0.3 %; on the other hand, the conversion treatment is not improved with a zinc ion concentration in excess of 2.5 %, while bath management becomes difficult and the economics are also undesirable.

The ferrous ion content should be 0.01 to 2.0 %, and an additional restriction also applies: that the ferrous ion/zinc ion ($\text{Fe}^{2+}/\text{Zn}^{2+}$) weight ratio should fall within the range of 0.005 to 3.0. Thus, when the zinc ion concentration is near its lower limit value of 0.3 %, the permissible ferrous ion based on the aforesaid weight ratio would calculate out to 0.00015 to 0.9 %. However, because the independent lower limit value for ferrous ion is 0.01 %, its content is in fact restricted to 0.01 to 0.9 %. On the other hand, when the zinc ion is at its upper limit value of 2.5 %, the ferrous ion content allowable under the constraint of its ratio to zinc ions would be 0.0125 to 7.5 %, but in fact the ferrous ion content must be restricted to 0.0125 to 2.0 % because of the independent upper limit value for this ion.

At ferrous ion concentrations below 0.01 %, the phosphate film obtained performs unsatisfactorily as a lubrica-

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tion base layer. Moreover, regulation of the iron concentration at such a low level in practice requires precipitation of iron by the frequent addition of an oxidant, such as NaNO_2 , H_2O_2 , or the like, that at the temperature used can fairly rapidly oxidize ferrous ions to ferric ions, which are less soluble in these solutions. This increases sludge production. Conversely, when the concentration of ferrous ions exceeds 2 %, a coarse, incomplete film tends to be formed, and poor film microstructure also results as a consequence of a substantial decline in the zinc content of the phosphate film, resulting from substitution of zinc by iron. The requirement for restricting the ferrous ions to zinc ions weight ratio as specified above arises from this consideration.

Phosphate ion (PO_4^{3-}) should be present at 0.5 to 5.0 %, with its optimal concentration being determined in part by the need to provide counter ions for the specified cations present in the solution. Poor quality film formation is encountered at phosphate ion concentrations below 0.5 %. On the other hand, while the use of more than 5.0 % of phosphate is possible, this serves primarily to increase the cost without improving film formation.

Nitrate ion (NO_3^-) is to be present at 0.7 to 12.0 %. At less than 0.7 %, the film formation rate slows, lengthening the treatment time, and the film obtained is coarse and poorly adherent. Exceeding 12.0 % nitrate causes an increase in the $\text{Zn}(\text{NO}_3)_2$ concentration in the treatment solution, which causes a low $\text{Zn}(\text{H}_2\text{PO}_4)_2/\text{Zn}(\text{NO}_3)_2$ ratio. This results in an unsatisfactory concentration of the $\text{Zn}(\text{H}_2\text{PO}_4)_2$ required for good film formation and thus a reduced conversion-coating capacity.

In addition to the preceding, the phosphate treatment solution used in the present invention also contains, as an essential component, 0.02 to 0.25 % of water-soluble, nitro and sulfonic group containing aromatic compound(s). Preferably these compounds are selected from the group of compounds containing a benzene, naphthalene, or anthracene

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nucleus with at least one each of a nitro and a sulfonic acid or sulfonate substituent on this nucleus. More preferably, the aromatic compounds are selected from the group consisting of nitrobenzene sulfonic acid, nitroaniline sulfonic acid, nitrotoluene sulfonic acid, nitroxylenesulfonic acid, and the salts of these acids, with meta-nitrobenzene sulfonic acid or its salts most preferred. Any of these compounds will serve to lower the treatment temperature for the iron-containing zinc phosphate treatment solution while also functioning to give a fine, dense phosphate film with relatively small crystalline particles. The treatment bath according to the present invention, having the above described composition, although containing iron, nevertheless can produce a fine, dense phosphate film with relatively small crystalline particles on the surface of iron and steel, with preferred coat weights of 7 to 12 grams per square meter (" g/m^2 "), through immersion or other contact for 3 to 20 minutes at the relatively low temperatures of 35 to 65 degrees Centigrade. This film forms a base layer adapted to severe cold-working operations. Moreover, because the zinc phosphate based treatment solution contains iron (Fe^{2+}), an accelerator such as NO_2^- or H_2O_2 is generally unnecessary, and preferably is not used in the phosphating solutions. As a result, one effect is the relatively slight precipitation of sludge, such as FePO_4 and/or $\text{Zn}_3(\text{PO}_4)_2$, from the phosphating solutions used in a process according to the invention.

When the aforementioned aromatic compound component is present at a concentration of less than 0.02 %, the beneficial effect deriving from its addition will either be insignificant or entirely absent. On the other hand, the beneficial effects of temperature reduction and development of a fine, dense phosphate film are no longer obtained to any greater degree at concentrations in excess of 0.25 %. In fact, the use of larger quantities hampers film formation.

If desired, the phosphate treatment solution according

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to the invention may contain a chelating agent for iron to increase the rate of phosphate film formation. When such a chelating agent is used, it is preferably present in an amount of from 0.01 to 0.05 % of the phosphating solution and is preferably selected from the group consisting of oxalic acid, citric acid, glycerophosphoric acid, urea, polyvinyl alcohol, and poly(vinyl pyrrolidone). Moreover, the phosphate treatment solution used in the present invention may contain chlorate ions from some constituent such as NaClO_3 as additional oxidizer, simple and/or complex fluoride ions, and heavy metal ions such as nickel, cobalt, copper, and the like.

As discussed above, the method of the present invention brings about the formation of a phosphate film on a clean iron or steel surface upon contact, preferably by immersion, for 3 to 20 minutes at 35 to 65 degrees Centigrade in a phosphate treatment solution with the components as specified above. This process according to the invention also preferably includes a water rinse and drying step or a water rinse and neutralization step after phosphate film formation, and the process further includes another step of lubricant treatment after phosphating and preferably after a water rinse and drying after phosphating. The lubricant treatment may contain any conventional lubricant such as molybdenum disulfide, tungsten disulfide, graphite, highly fluorinated organic resin, or an oil lubricant which contains an extreme pressure additive. Most preferred, however, is the lubricating treatment comprising the formation of a zinc/fatty acid film and an alkali metal/fatty acid film in layers over the phosphate film by immersion with heating to 70 to 75 degrees Centigrade in a weakly alkaline aqueous metal soap solution based on the alkali metal salts of C_{16} to C_{18} saturated and/or unsaturated fatty acids, most preferably sodium stearate.

The final step in a method according to the invention generally is that of drying the lubricant film.

When the phosphating solution used according to the

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invention does not contain calcium, the film formed by phosphating contains mainly phosphophyllite ($\text{Zn}_2\text{Fe}(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$) crystals. When the treatment solution contains calcium ions in the quantity specified above, a uniform, microparticulate film is formed in which the main component is scholzite ($\text{Zn}_2\text{Ca}(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$) but also contains some phosphophyllite and hopeite ($\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$) with the same approximate size as the scholzite crystals. However, when less than 0.2 % calcium ions are present or when their weight ratio with zinc ions is less than 0.7, crystals larger than those of the scholzite system, thought to be phosphophyllite, become an important secondary crystal phase. Because the size of the phosphophyllite type crystals increases as the weight ratio of calcium ions to zinc ions declines, the crystalline structure of the film becomes nonuniform. Since a microhomogeneous film is a particular requirement for severe cold-working operations, such an inhomogeneous film is undesirable as the base layer for severe cold-working operations. Conversely, when the Ca ion content exceeds 2.0 % or when $\text{Ca}^{2+}/\text{Zn}^{2+}$ exceeds 4.0, relatively soft monetite (CaHPO_4) precipitates among the aforementioned microparticulate crystal types; this reduces the cold-workability.

The concentrations of zinc and ferrous ions for phosphating solutions with calcium according to the invention are preferred to be within the same ranges as for solutions without calcium, although in some cases the adverse consequences of concentrations outside the preferred ranges are different in the presence of calcium. For example, with zinc ion concentrations less than 0.3 %, relatively soft monetite tends to coprecipitate in the conversion film. At greater than 2.5 % of zinc ions, coprecipitated crystals of hopeite ($\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$) and phosphophyllite tend to be dispersed in the aforementioned scholzite crystals, readily leading to heterogeneity in the crystalline structure of the film. Moreover, at less than 0.01 % total concentration of ferrous ions or when the Fe^{2+} to Zn^{2+} ratio

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falls below 0.005, the film obtained tends to be unsatisfactory as a lubrication base layer adapted to severe cold-working operations. On the other hand, when the ferrous ion concentration exceeds 2.0 % or when $\text{Fe}^{2+}/\text{Zn}^{2+}$ exceeds 3.0, there is a decline in the zinc and calcium content in the phosphate films due to the excess iron fraction in the treatment solution, causing a poor coating formation or the formation of a coarse film of Fe-Hureaulith ($\text{Fe}_5\text{H}_2(\text{PO}_4)_4 \cdot 4\text{H}_2\text{O}$)-containing scholzite crystals.

The practice of the invention may be further appreciated from the following, non-limiting, examples and comparative examples.

Examples and Comparative Examples

Examples and Comparative Examples 1 to 4

Cylindrical test specimens of type S35C steel were pickled, rinsed with water, treated with phosphate treatment solution as described in Table 1, then dipped in 70 g/L soap lubricant (Palube® 235 from Nihon Parkerizing Company, Limited; main component, sodium stearate; auxiliary components, sodium borate and sodium nitrite) at 75 degrees Centigrade for 5 minutes and then dried. The coating weights of both phosphate and metallic lubricant obtained are shown in Table 2. The lubrication was then evaluated by backward punch extrusion under the following conditions:

The critical punch depth for the development of seizure was determined using backward punch extrusion as reported by Danmo, et al. (of the Toyota Central Research Laboratory) in Sosei to Kako [Journal of the Japan Society for the Technology of Plasticity], Volume 24, Number 265. This method is briefly described below.

Equipment and Test Conditions

A 200 ton cold-forging crank press made by Fukui Kikai Kabushiki Kaisha was used at a rate of 30 strokes per minute. Workpieces to be tested were made of type SKD11 steel, which is described in detail in

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Table 1. Composition of Phosphate Coating Treatment Solutions

components	examples				comparison examples			
	1	2	3	4	1	2	3	4
zinc ion (%)	0.7	0.7	0.7	0.3	0.2	0.7	0.7	0.7
calcium ion (%)	-	-	1.1	1.1	-	-	1.1	-
iron ion (%)	0.8	0.05	0.5	0.02	0.9	-	2.4	-
$\frac{\text{iron ion (\%)}}{\text{zinc ion (\%)}}$	1.14	0.07	0.7	0.07	4.5	-	3.4	-
$\frac{\text{calcium ion (\%)}}{\text{zinc ion (\%)}}$	-	-	1.57	3.67	-	-	1.57	-
phosphate ion (%)	1.0	2.0	1.0	1.8	1.2	2.0	1.8	1.0
nitrate ion (%)	3.8	4.7	2.5	2.4	1.6	4.9	2.4	1.5
m-nitrobenzene-sulfonate ion (%)	0.05	-	0.05	-	0.05	-	0.05	0.05
nitroxylenesulfonate ion (%)	-	0.03	-	0.07	-	0.03	-	-
nitrite ion (%)	-	-	-	-	-	0.005	-	0.01
treatment temperature (°C)	50	50	50	60	50	50	50	50
treatment time (minutes)	10	4	10	5	10	4	10	10

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Table 2 Weight of Produced Coating and Quantity of Metal Soap

	No.	weight of phosphate film g/m ²	quantity of metal soap g/m ²
examples	1	9.4	3.7
	2	8.2	3.5
	3	9.1	2.6
	4	8.0	2.2
comparison examples	1	4.0	1.5
	2	7.5	1.9
	3	15.0	1.7
	4	6.8	1.5

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Japanese Industrial Standard G - 4404. The punch used to deform the workpieces was made of Hitachi Metals' high-speed tool steel type HAP40 (made by powder metallurgical methods and containing in percents by weight: C = 1.3, Cr = 4.0, W = 6.0, Mo = 5.0, V = 3.0, and Co = 8.0). The test method may be further appreciated with the aid of Figures 2 and 3. Figure 2 shows a cross section of part of the test machinery with a test in progress. A load cell 1 applies pressure through a punch holder 2 to the punch 3. The punch 3 forces a workpiece 6 to deform as it forms a hollow space in the originally solid cylindrical workpiece while pushing it through a cylindrical hole in the die 4 that has a diameter slightly smaller than that of original workpiece. When the test is completed, the deformed workpiece is ejected through the top of the die by the knockout punch 5. A strain gauge 7 monitors the mechanical force being used in the deformation.

The shape of the punch is shown in greater detail in Figure 3a. The main shaft of the punch has a diameter of 20.8 millimeters ("mm"), but the leading edge has a diameter of 21.2 mm and is rounded as shown in the Figure, with a radius of curvature of not less than 0.5 mm at any point and a very smooth finish (meeting the standards described in Japanese Industrial Standard B0601 for marking with the symbol of four equilateral triangles with adjacent bases) on all parts of the punch which come into contact with the workpiece during the testing process. The workpiece initially has a height (dimension H in Figure 3b) of from 18 - 40 mm and has a diameter (dimension D in Figure 3b) of 30 mm. The production of a centered hole with a diameter of 21.2 mm in the workpiece during testing therefore causes a horizontal cross sectional area reduction of 50 % in the workpiece. As shown in vertical cross section in Figure 3c, a

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section 10 mm in length at the bottom of the workpiece remains without any center hole.

5 The results of the tests of critical depth for seizure generation are shown in Figure 1. The critical depth for seizure generation was greater in the examples than in the comparison examples, indicating a superior lubricating performance for the examples. A satisfactory amount of phosphate coating and metal soap quantity are also obtained in Examples 1 to 4, as shown in Table 2.

10 Examples and Comparative Examples 5 to 8

15 Samples 10 mm in diameter by 100 mm long of wire rod of type S-45C steel were pickled, rinsed with water, treated with a phosphate treatment solution as described in Table 3, rinsed again with water, immersed for 5 minutes at 75 degrees Centigrade in 70 g/L of the soap lubricant Palube® 235, and then dried. Using a Bowden frictional abrasion tester (Model EFM-4 from Toyo Baldwin Kabushiki Kaisha), the number of strokes until seizure was measured under the conditions shown in Table 4, with a coefficient of friction ≥ 0.2 . The coating weights of phosphate and metal soap obtained are shown in Table 5 and the results of the frictional abrasion test are reported in Table 6. As Tables 5 and 6 make clear, satisfactory coating quantities were obtained in Examples 5 through 8, and the Bowden test results demonstrate that the seizure resistance is far superior to that in Comparison Examples 5 through 8.

25 Benefits of the Invention

As explained above, the lubrication treatment method of the present invention achieves the following benefits:

30 An efficient treatment with an immersion treatment time of 3 to 20 minutes can be used at a relatively low temperature of 35 to 65 degrees Centigrade.

The use of a strong accelerator such as NaNO_2 or H_2O_2 can be avoided, so that management of the treatment solution is facilitated.

35 A dense, fine phosphate coating with a coating weight

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of 7 to 12 g/m² is formed and provides an optimal base layer for severe cold-working.

The treatment solution develops only a small quantity of sludge.

- 5 The lubricant film obtained by implementing the present invention has excellent cold-working properties. In particular, the coating obtained has very good properties when a metal soap film layer is formed on the phosphate coating using a lubricant treatment solution comprising an
- 10 aqueous treatment solution based on the alkali metal salt of saturated or unsaturated C₁₆ to C₁₈ fatty acid, particularly sodium stearate.

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Table 3. Composition of Phosphate Coating Treatment Solutions

components	examples				comparison examples			
	5	6	7	8	5	6	7	8
zinc ion (%)	0.5	1.5	2.0	0.4	0.3	1.0	0.7	0.7
calcium ion (%)	-	-	1.5	0.8	1.5	0.9	-	0.6
iron ion (%)	1.5	0.01	0.01	1.0	0.02	-	-	-
$\frac{\text{iron ion (\%)}}{\text{zinc ion (\%)}}$	3.0	0.007	0.005	2.5	0.07	-	-	-
$\frac{\text{calcium ion (\%)}}{\text{zinc ion (\%)}}$	-	-	0.75	2.0	5.0	0.9	-	0.86
phosphate ion (%)	2.9	1.7	4.5	2.0	2.4	1.4	1.0	1.2
nitrate ion (%)	9.6	5.0	8.0	5.4	2.7	2.1	1.5	1.8
m-nitrobenzene-sulfonate ion (%)	0.1	0.07	0.2	0.1	0.03	0.05	-	-
nitrite ion (%)	-	-	-	-	-	0.01	0.01	0.01
treatment temperature (°C)	60	40	40	60	60	50	80	80
treatment time (minutes)	5	7	4	7	5	10	5	5

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Table 4. Bowden Test Conditions

pressure element	SUJ-2, 5 mm ϕ
load	5 kg
sliding width	10 mm
sliding velocity	10 mm/sec
sliding temperature	25°C

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Table 5.

	No.	weight of phosphate film g/m^2	quantity of metal soap g/m^2
examples	5	11.0	3.4
	6	10.5	3.6
	7	11.3	2.8
	8	9.4	3.1
comparison examples	5	3.9	0.8
	6	4.8	0.7
	7	7.5	1.9
	8	6.8	1.7

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Table 6.

	No.	number of strokes until seizure
examples	5	2200
	6	2400
	7	2900
	8	2100
comparison examples	5	1500
	6	1200
	7	1700
	8	1900

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What is claimed is:

CLAIMS

- 1 1. A process for applying a lubricating layer to the sur-
2 faces of iron and steel objects by first applying a phos-
3 phate layer over the surfaces and subsequently applying a
4 lubricating layer over the phosphating layer, wherein the
5 improvement comprises applying the phosphating layer by
6 contact for about 3 to about 20 minutes at a temperature in
7 the range from about 35 to about 65 degrees Centigrade bet-
8 ween the iron and steel surfaces and an aqueous phosphating
9 solution comprising, in percentages by weight:
- 10 (A) from about 0.3 to about 2.5 % of zinc ions;
11 (B) from about 0.01 to about 2.0 % of ferrous ions;
12 (C) from about 0.5 to about 5.0 % of phosphate ions;
13 (D) from about 0.7 to about 12.0 % of nitrate ions; and
14 (E) from about 0.02 to about 0.25 % of molecules selected
15 from the group consisting of (i) aromatic organic mol-
16 ecules each having at least one nitro group substitu-
17 ent and at least one sulfonic acid substituent on an
18 aromatic ring and (ii) sulfonate salts of molecules of
19 type (i),
20 the weight ratio of ferrous ions to zinc ions in said phos-
21 phating solution being in the range from about 0.005 to
22 about 3.0.
- 1 2. A process according to claim 1, wherein component (E)
2 is selected from the group consisting of nitrobenzene sul-
3 fonic acid, nitrotoluene sulfonic acid, nitroaniline sul-
4 fonic acid, nitroxylen sulfonic acid, and salts of any of
5 these acids.
- 1 3. A process according to claim 2, wherein component (E)
2 is selected from meta-nitrobenzene sulfonic acid and its
3 salts.

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- 1 4. A process according to claim 3, wherein said phosphat-
2 ing solution additionally comprises from about 0.2 to about
3 2.0 % by weight of calcium ions and the weight ratio of
4 calcium ions to zinc ions in the composition is in the
5 range from about 0.7 to about 4.0.
- 1 5. A process according to claim 2, wherein said phosphat-
2 ing solution additionally comprises from about 0.2 to about
3 2.0 % by weight of calcium ions and the weight ratio of
4 calcium ions to zinc ions in the composition is in the
5 range from about 0.7 to about 4.0.
- 1 6. A process according to claim 1, wherein said phosphat-
2 ing solution additionally comprises from about 0.2 to about
3 2.0 % by weight of calcium ions and the weight ratio of
4 calcium ions to zinc ions in the composition is in the
5 range from about 0.7 to about 4.0.
- 1 7. A process according to claim 6, wherein the lubricat-
2 ing layer is applied by contact with a weakly alkaline a-
3 queous solution of materials selected from the group con-
4 sisting of salts of saturated and unsaturated fatty acids
5 having from 16 to 18 carbon atoms per molecule.
- 1 8. A process according to claim 5, wherein the lubricat-
2 ing layer is applied by contact with a weakly alkaline a-
3 queous solution of materials selected from the group con-
4 sisting of salts of saturated and unsaturated fatty acids
5 having from 16 to 18 carbon atoms per molecule.
- 1 9. A process according to claim 4, wherein the lubricat-
2 ing layer is applied by contact with a weakly alkaline a-
3 queous solution of materials selected from the group con-
4 sisting of salts of saturated and unsaturated fatty acids
5 having from 16 to 18 carbon atoms per molecule.
- 1 10. A process according to claim 3, wherein the lubricat-
2 ing layer is applied by contact with a weakly alkaline a-
3 queous solution of materials selected from the group con-
4 sisting of salts of saturated and unsaturated fatty acids
5 having from 16 to 18 carbon atoms per molecule.

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- 1 11. A process according to claim 2, wherein the lubricat-
2 ing layer is applied by contact with a weakly alkaline a-
3 queous solution of materials selected from the group con-
4 sisting of salts of saturated and unsaturated fatty acids
5 having from 16 to 18 carbon atoms per molecule.
- 1 12. A process according to claim 1, wherein the lubricat-
2 ing layer is applied by contact with a weakly alkaline a-
3 queous solution of materials selected from the group con-
4 sisting of salts of saturated and unsaturated fatty acids
5 having from 16 to 18 carbon atoms per molecule.
- 1 13. A process according to claim 12, wherein the lubricat-
2 ing layer is applied by contact with a solution consisting
3 essentially of water, sodium stearate, sodium borate, and
4 sodium nitrite.
- 1 14. A process according to claim 11, wherein the lubricat-
2 ing layer is applied by contact with a solution consisting
3 essentially of water, sodium stearate, sodium borate, and
4 sodium nitrite.
- 1 15. A process according to claim 10, wherein the lubricat-
2 ing layer is applied by contact with a solution consisting
3 essentially of water, sodium stearate, sodium borate, and
4 sodium nitrite.
- 1 16. A process according to claim 9, wherein the lubricat-
2 ing layer is applied by contact with a solution consisting
3 essentially of water, sodium stearate, sodium borate, and
4 sodium nitrite.
- 1 17. A process according to claim 8, wherein the lubricat-
2 ing layer is applied by contact with a solution consisting
3 essentially of water, sodium stearate, sodium borate, and
4 sodium nitrite.
- 1 18. A process according to claim 7, wherein the lubricat-
2 ing layer is applied by contact with a solution consisting
3 essentially of water, sodium stearate, sodium borate, and
4 sodium nitrite.

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- 1 19. A process according to claim 16, wherein said phosphat-
- 2 hating solution is substantially free from nitrite ions and
- 3 hydrogen peroxide.
- 1 20. A process according to claim 1, wherein said phosphat-
- 2 ing solution is substantially free from nitrite ions and
- 3 hydrogen peroxide.

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Figure 1.

	NO	critical punch depth for seizure (mm)						
		0	10	20	30	40	50	60
examples	1							
	2							
	3							
	4							
comparison examples	1							
	2							
	3							
	4							

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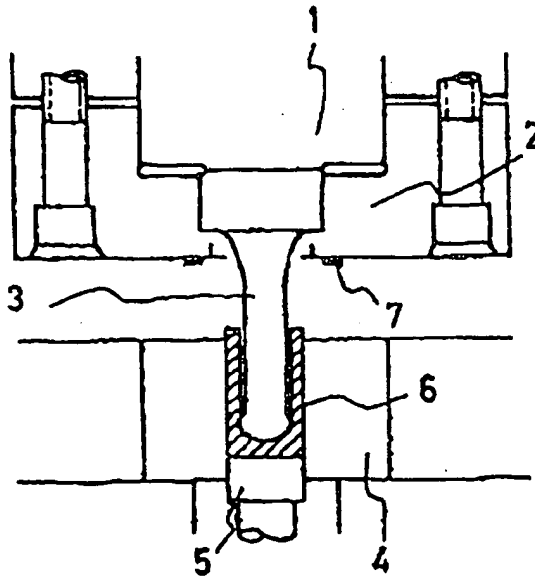


Figure 2.

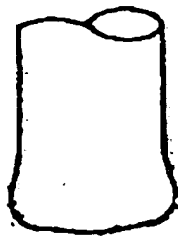


Figure 3a

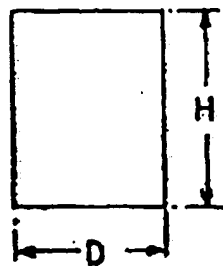


Figure 3b

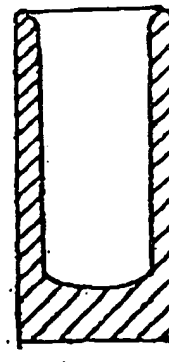


Figure 3c

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